

Efficient Singlet Fission in Nanoparticle of Amphipathic Anthracene-Tetracene Dyad with Broadband Light Harvesting Ability

Xinyu Nie[#], Heyuan Liu[#], Weijie Wang, Pengkun Su, Jun Zhou, Zhi Li, Zhaobin Liu,
Zhaofeng Tang, Yanli Chen, and Xiyu Li*

Content

1. Dynamic light scattering experiment	2
2. Comparison between absorption spectrum of DPA and fluorescence spectrum of DPT	3
3. <i>fs</i> -TA spectra of DPA and DPT in THF	4
4. <i>fs</i> -TA spectra of DPT-DPA-COOH in THF excited at 460 nm	6
5. Sensitization experiment of DPT-DPA-COOH nanoparticle	7
6. Comparison of the triplet spectrum obtained from SF and sensitization experiment 9	
7. <i>fs</i> -TA spectra of DPT-DPA-COOH in nanoparticle excited at 460 nm	10
8. Comparison of the raw data and the fitting result obtained from the global analysis 11	
9. Determination of the triplet state yield of DPT-DPA-COOH nanoparticle	13
Reference	15

1. Dynamic light scattering experiment

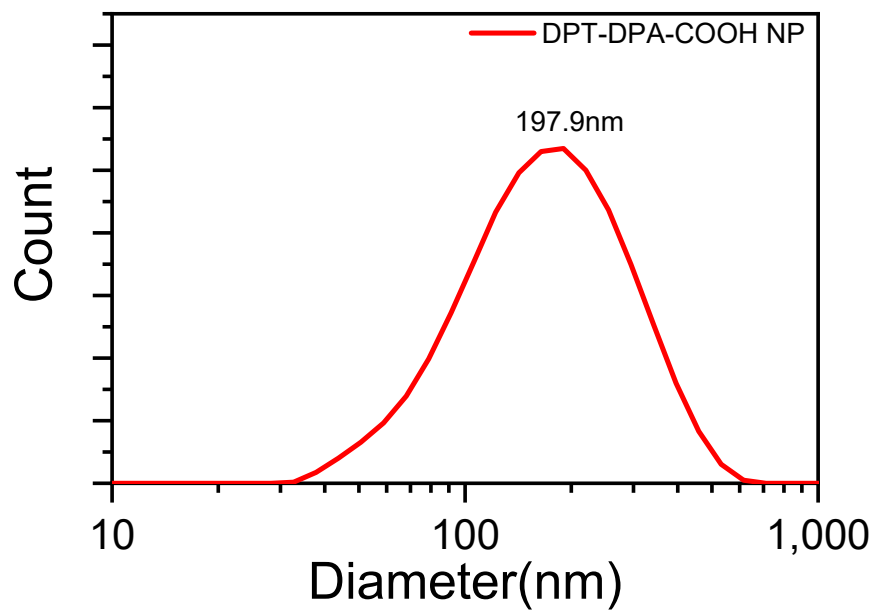


Figure S1. Nanoparticle size distribution of DPT-DPA-COOH NP.

2. Comparison between absorption spectrum of DPA and fluorescence spectrum of DPT

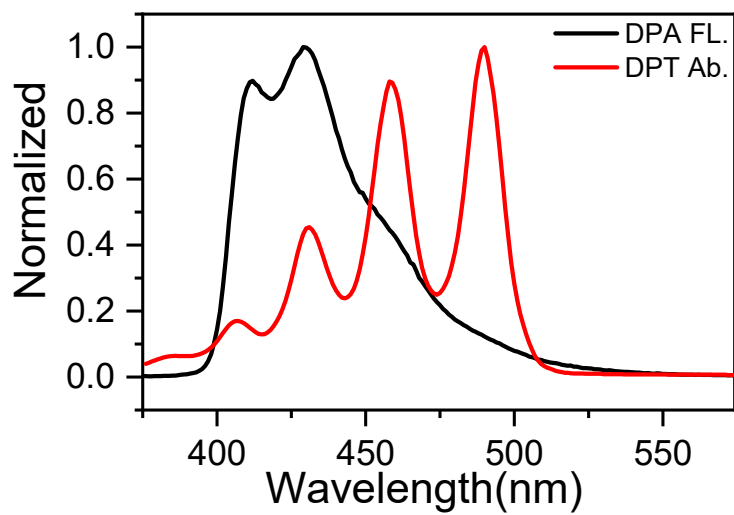


Figure S2. Comparison between absorption spectrum of DPA and fluorescence spectrum of DPT.

3. *fs*-TA spectra of DPA and DPT in THF

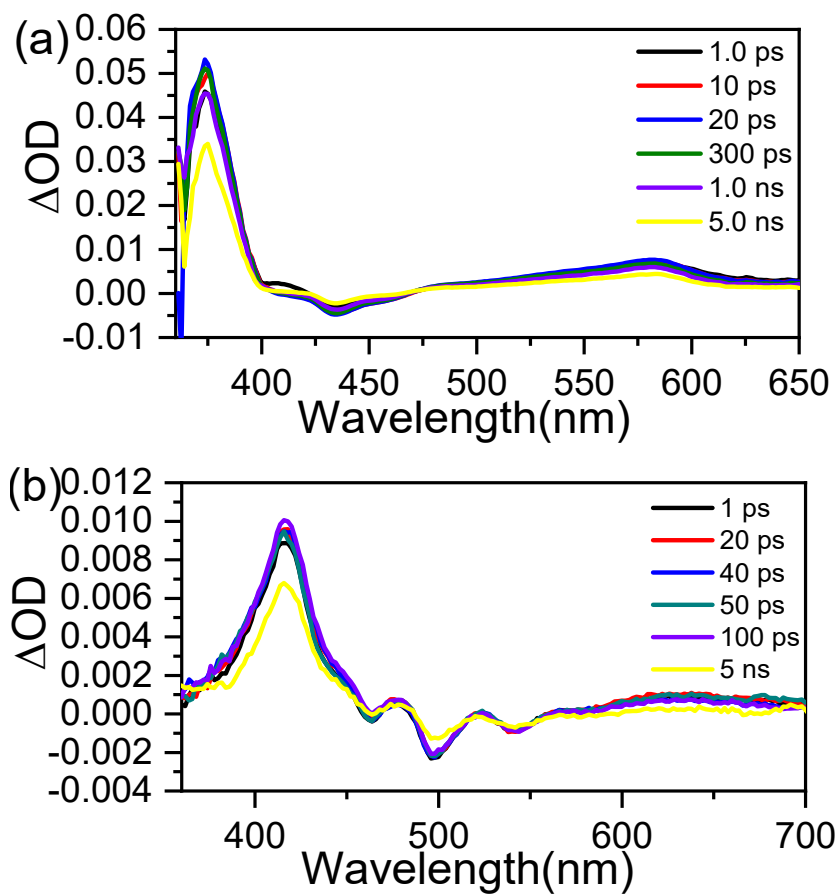


Figure S3. *fs*-TA spectra of DPA and DPT in THF excited at 360 nm and 460 nm, respectively.

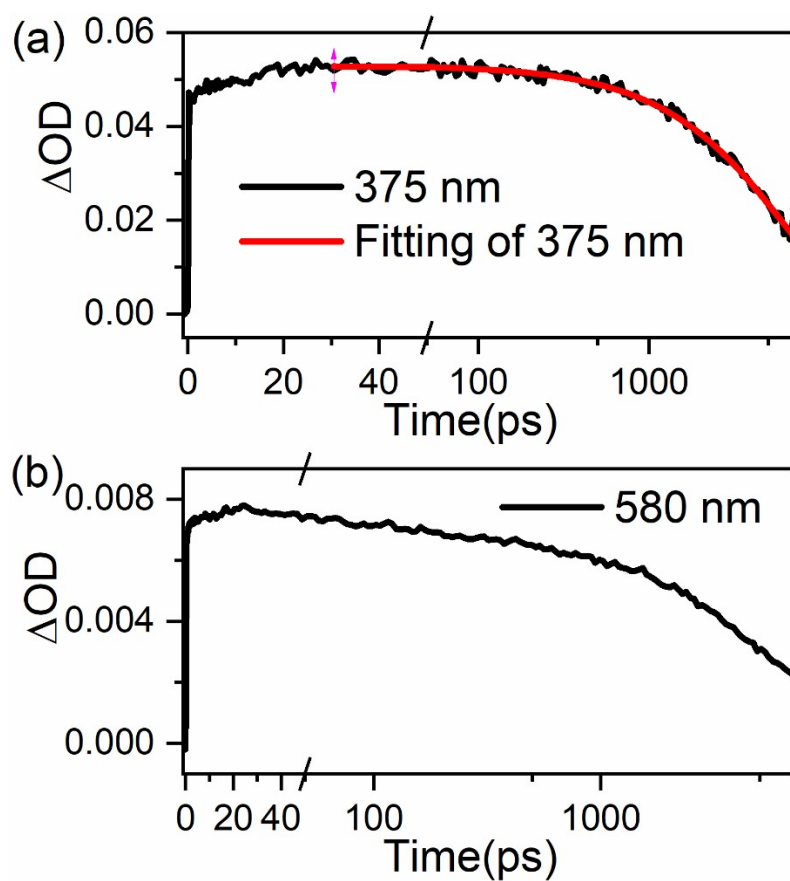


Figure S4. Single-wavelength dynamics of DPA in THF probed at 375 and 580 nm.

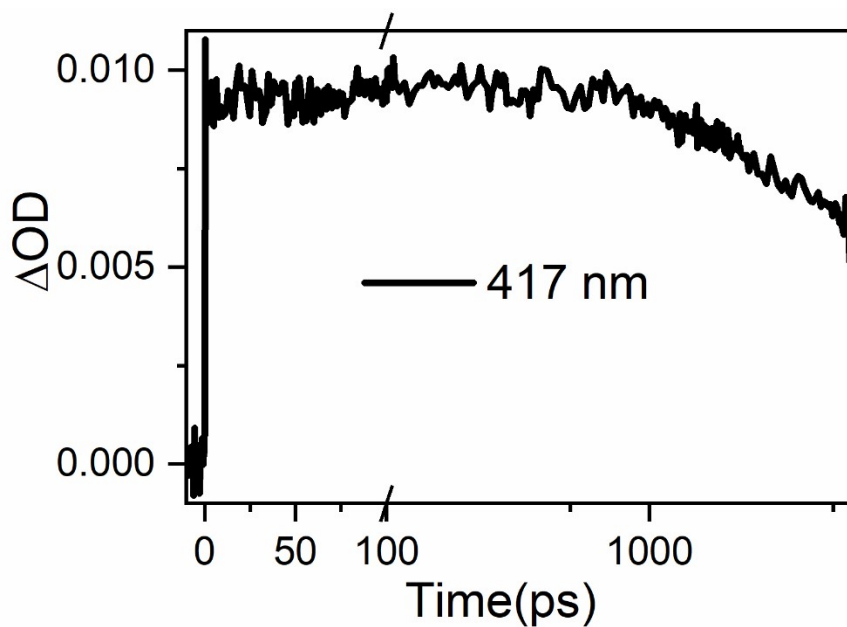


Figure S5. Single-wavelength dynamics of DPT in THF probed at 417 nm.

4. *fs*-TA spectra of DPT-DPA-COOH in THF excited at 460 nm

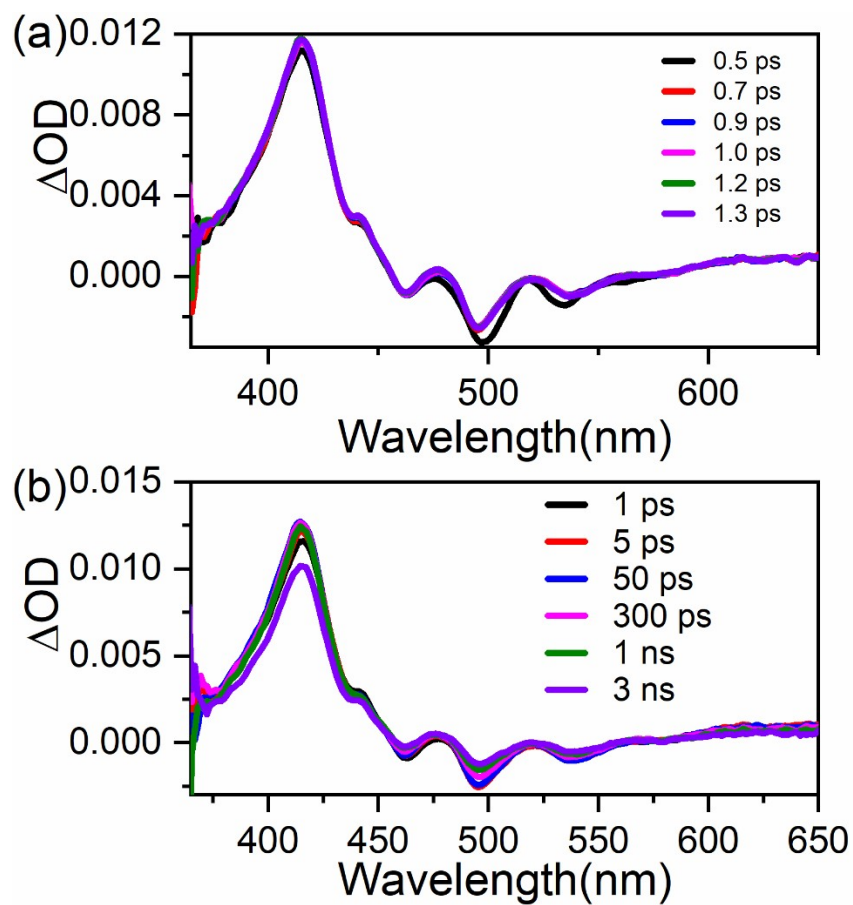


Figure S6. *fs*-TA spectra of DPT-DPA-COOH in THF excited at 460 nm.

5. Sensitization experiment of DPT-DPA-COOH nanoparticle

To obtain the triplet spectral signature of DPT-DPA-COOH nanoparticle, triplet sensitization of DPT-DPA-COOH suspension was performed with the known triplet sensitizer, platinumoctaethylporphyrin (PtOEP). The triplet sensitization nanoparticle sample was prepared by adding 0.4 mL THF solution of 1.4 mg of DPT-DPA-COOH and 0.2 mg of PtOEP to a vigorously stirred deionized water (10 mL). The triplet sensitization sample is prepared in glovebox and all the solvents are degassed first by Freeze-Pump-Thaw method. Photoexcitation of the PtOEP excited at 535 nm results in rapid intersystem crossing followed by triplet energy transfer to DPT-DPA-COOH (Figure S7). At initial times, the T_1 - T_n absorption (424 nm) and the ground-state bleaching (GSB) (387 nm) of PtOEP were observed (Figure S7).^{1,2} As the time delay, the triplet absorption of PtOEP centered at 424 nm decayed almost completely in hundreds of picoseconds. Meanwhile, the GSB band of PtOEP at 387 nm was also decreased significantly. A new spectral feature with the main absorption band at 494 nm emerges, which can be assigned to the T_1 state of diphenyl substituted tetracene based on the previous report.^{1,2}

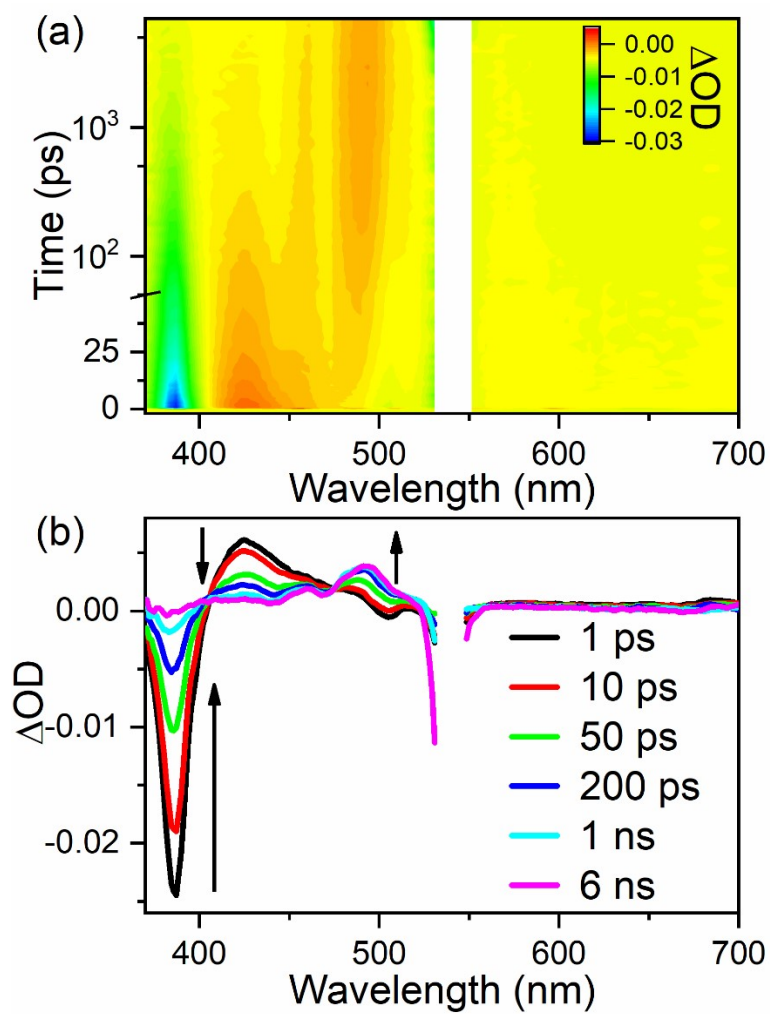


Figure S7. *fs*-TA spectra of nanoparticle of the mixture between DPT-DPA-COOH and PtOEP in water suspension excited at 535 nm.

6. Comparison of the triplet spectrum obtained from SF and sensitization experiment

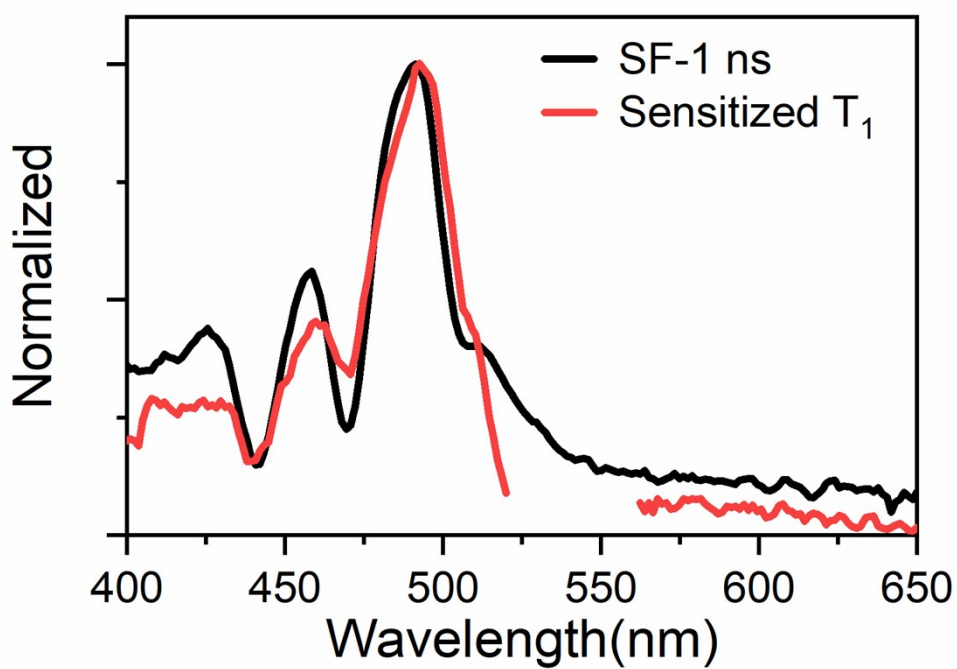


Figure S8. Comparison of the triplet spectrum obtained from SF and sensitization experiment.

7. *fs*-TA spectra of DPT-DPA-COOH in nanoparticle excited at 460 nm

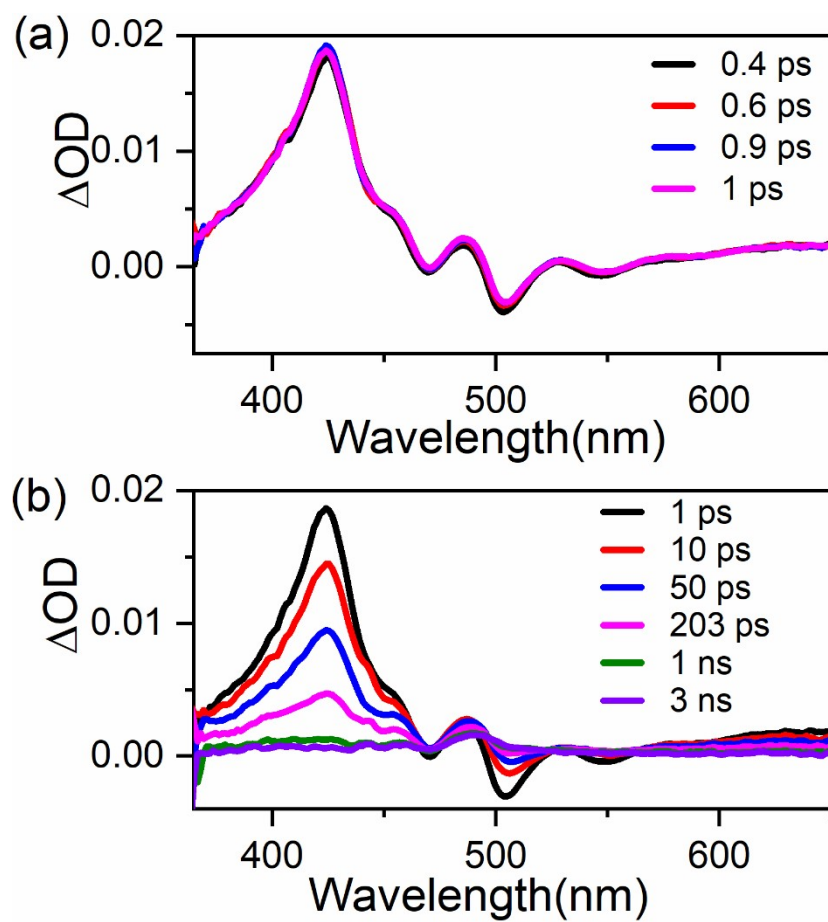


Figure S9. *fs*-TA spectra of DPT-DPA-COOH in nanoparticle excited at 460 nm.

8. Comparison of the raw data and the fitting result obtained from the global analysis

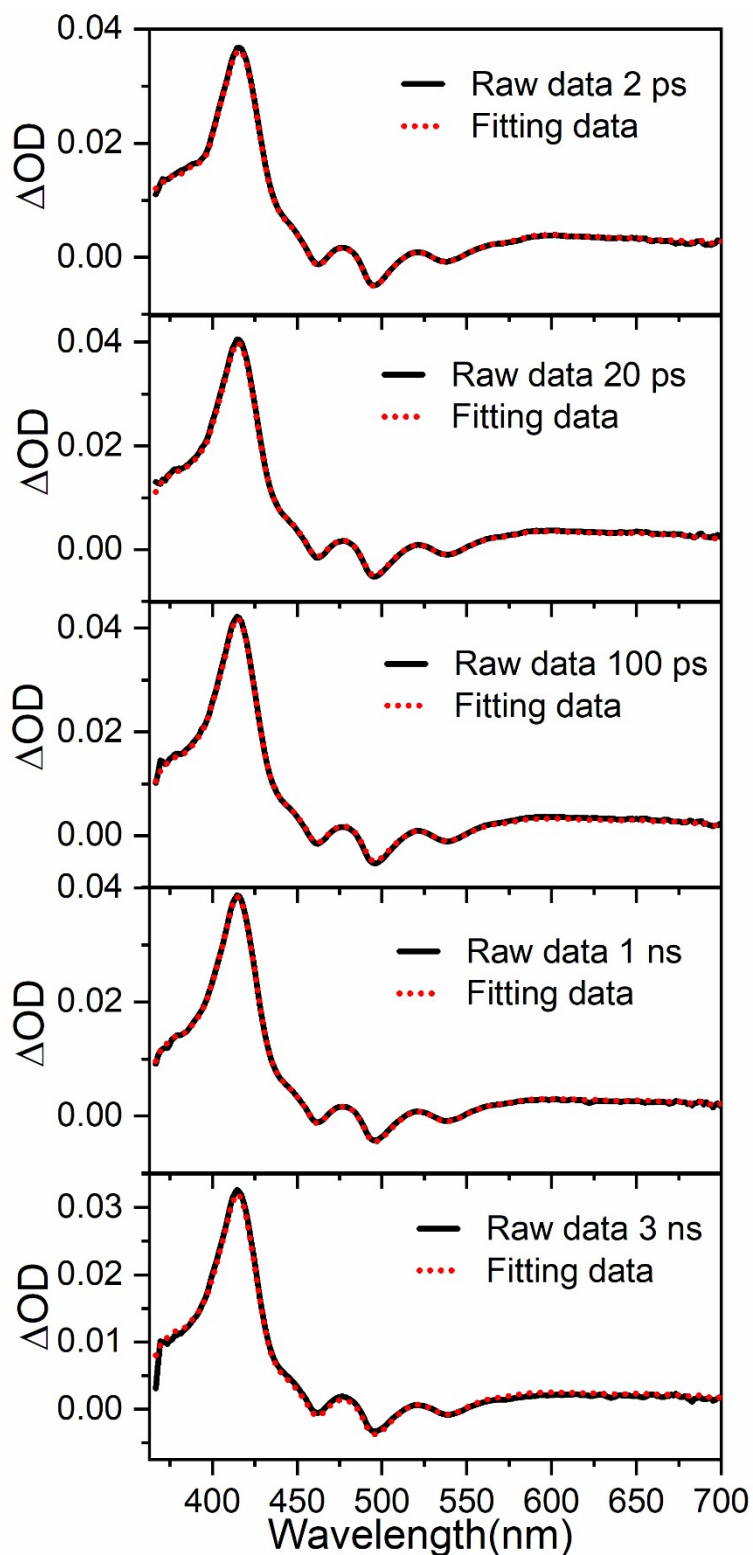


Figure S10. Comparison between the raw data and the fitting result obtained from the global analysis for DPT-DPA-COOH in THF solution.

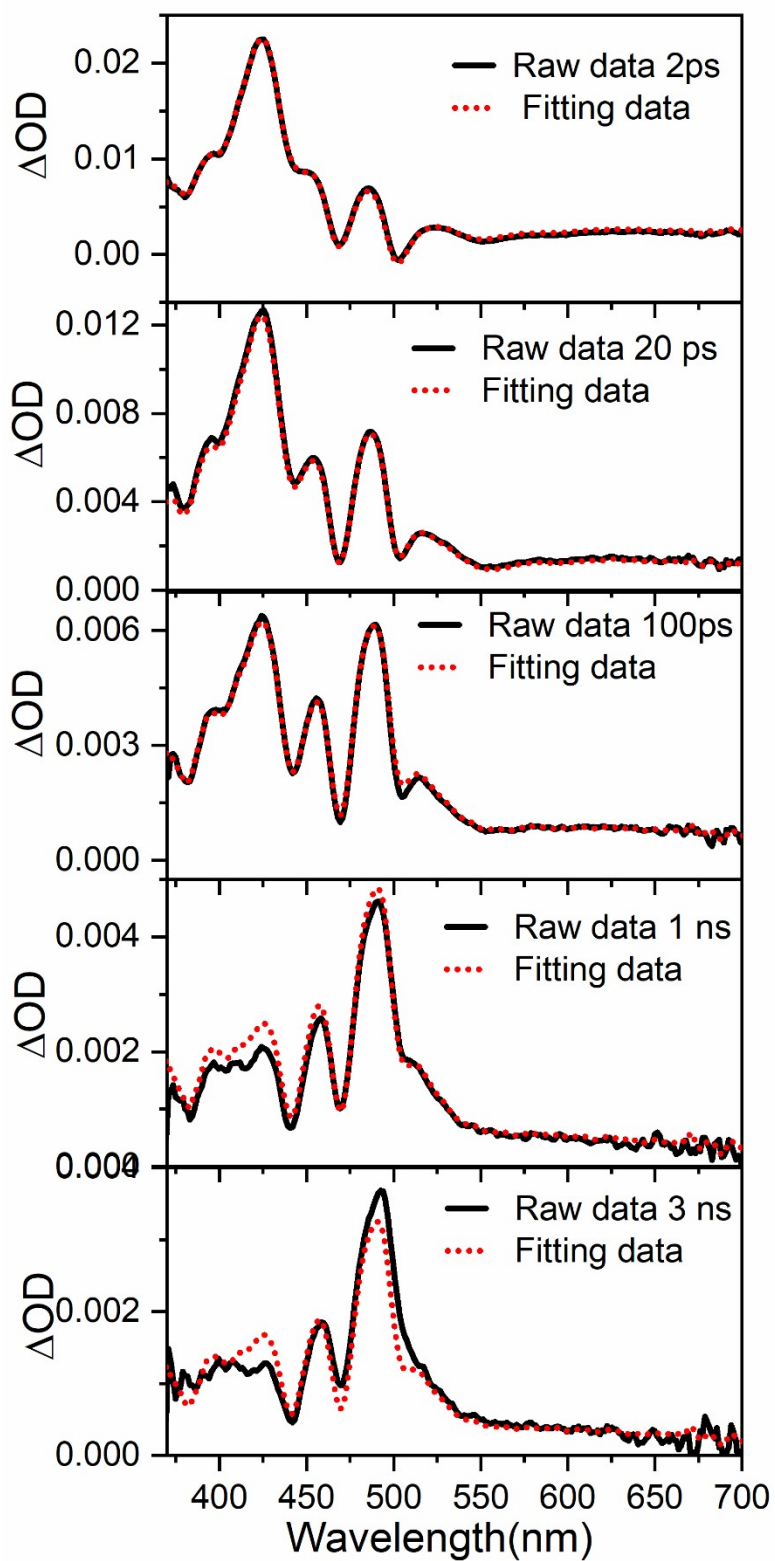


Figure S11. Comparison between the raw data and the fitting result obtained from the global analysis for DPT-DPA-COOH nanoparticle.

9. Determination of the triplet state yield of DPT-DPA-COOH nanoparticle

As the literature report, an early time trace (0.5 ps) after photoexcitation for DPT-DPA-COOH NP, the S_1 concentration is assumed C_1 whereas the T_1 concentration remains nearly 0. At initial time, the S_0 concentration is C_0 .

$$\Delta C = S_1(0.5 \text{ ps}) - S_0 = (C_0 - C_1 - 0) - C_0 = -C_1 = -C(S_1)$$

At 1358 ps, S_1 depopulates fully as a result of efficient SF and T_1 generates according to the global fitting result.

$$\Delta C(1358 \text{ ps}) = (C_0 - 0 - C(T_1)) - C_0 = -C(T_1)$$

Therefore, the triplet yield of DPT-DPA-COOH NP can be obtained from the following equation:

$$\Phi_{T_1} = \frac{C(T_1)}{C(S_1)} = -\frac{\Delta C(1358 \text{ ps})}{-\Delta C(0.5 \text{ ps})} = \frac{GSB(1358 \text{ ps})}{GSB(0.5 \text{ ps})}$$

Therefore, the triplet yield is actually proportional to the intensity of the pure GSB as the transient absorption spectra show the superposition of GSB, S_1 absorption or T_1 absorption. Thus, proper substraction of the scaled GSB spectrum can reproduce the pure S_0 , S_1 , T_1 spectra and their respective pure GSB. The specific operation is that only enough ground state absorption is added to the transient trace in order to remove the extremum at 499 nm, 467 nm in DPT-DPA-COOH NP (Figure S12 and S13). Therefore, the SF efficiencies and triplet yields can be determined ($110 \pm 10\%$).

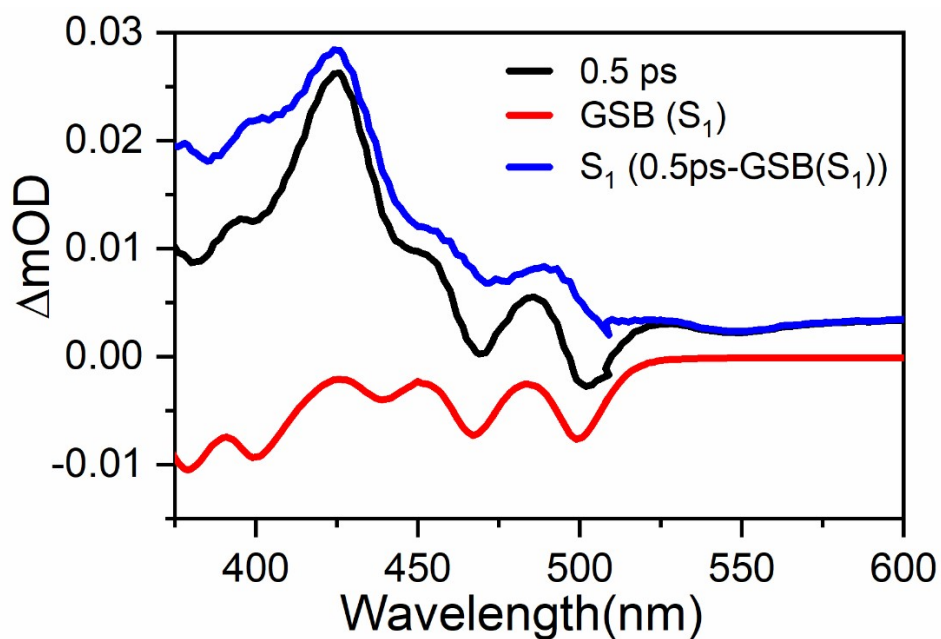


Figure S12. TA spectra and subtraction of the scaled steady state absorption spectra and resulting reconstructed absorption spectra of the pure singlet state of DPT-DPA-COOH NP.

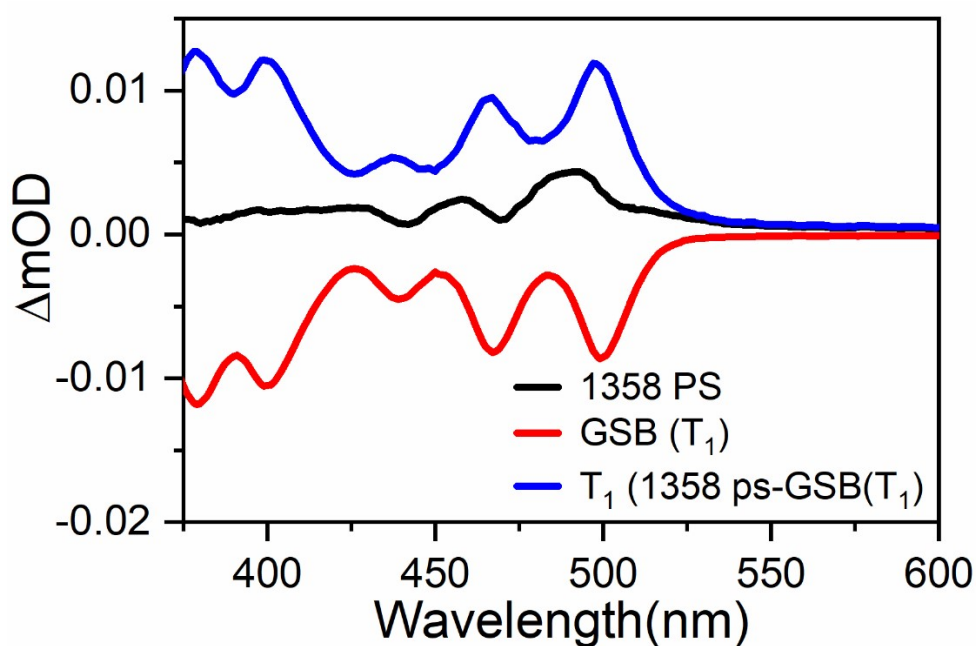


Figure S13. TA spectra and subtraction of the scaled steady state absorption spectra and resulting reconstructed absorption spectra of triplet state of the DPT-DPA-COOH NP.

Reference

1. H. Liu, R. Wang, L. Shen, Y. Xu, M. Xiao, C. Zhang and X. Li, *Org. Lett.*, 2017, **19**, 580-583.
2. H. Liu, Z. Wang, X. Wang, L. Shen, C. Zhang, M. Xiao and X. Li, *J. Mate. Chem. C*, 2018, **6**, 3245-3253